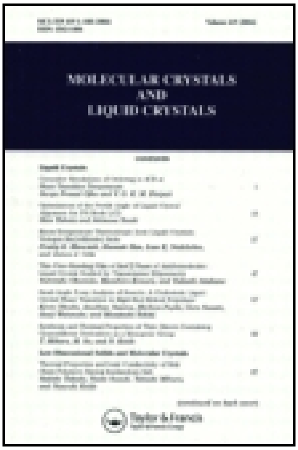

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

New Theories for Smectic and Nematic Liquid-Crystal Polymers: Backbone Lcps and Their Mixtures and Side-Chain Lcps

F. Dowell [a]

[a] Theoretical Division, Los Alamos National Laboratory, University of California, Los, Alamos, NM, 87545, USA

To cite this article: F. Dowell (1988): New Theories for Smectic and Nematic Liquid-Crystal Polymers: Backbone Lcps and Their Mixtures and Side-Chain Lcps, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 157:1, 203-227

To link to this article: http://dx.doi.org/10.1080/00268948808080234

Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt., 1988, Vol. 157, pp. 203–227
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Printed in the United States of America

NEW THEORIES FOR SMECTIC AND NEMATIC LIQUID-CRYSTAL POLYMERS: BACKBONE LCPS AND THEIR MIXTURES AND SIDE-CHAIN LCPS

F. DOWELL
Theoretical Division, Los Alamos National Laboratory,
University of California, Los Alamos, NM 87545 USA

Abstract A summary of predictions and explanations from new statistical-physics theories for both backbone and side-chain liquid crystalline polymers (LCPs) and for mixtures with backbone LCPs are presented. Trends in thermodynamic and molecular ordering properties have been calculated as a function of pressure, density, temperature, and molecule chemical structures (including degree of polymerization and the following properties of the chemical structures of the repeat units: lengths and shapes, intra-chain rotation energies, dipole moments, site-site polarizabilities and Lennard-Jones potentials, etc.) in nematic and multiple smectic-A LC phases and in the isotropic liquid phase. The theoretical results are found to be in good agreement with existing experimental data. These theories can also be applied to combined LCPs. Since these theories have no ad hoc or arbitrarily adjustable parameters, these theories can be used to design new LCPs and new solvents as well as to predict and explain properties.

INTRODUCTION

Liquid crystalline polymers (LCPs) are of considerable basic and applied interest (see the general background sources in Ref. 1). From a basic standpoint, LCPs in condensed phases constitute one of the most challenging many-body problems in statistical physics--that is, the packing of many changing, very anisotropic shapes.

In backbone LCPs, the low-molecular-weight (LMW) liquid-crystal (LC) structure is repeated many times to make the polymer chain or backbone. In side-chain LCPs, LMW LC structures are attached as side chains to a non-LC polymer backbone (such as polyethylene), with the side chains resembling the teeth of a brush or comb. In combined LCPs, each molecule is a backbone LCP with LC side-chains.

Some backbone LCPs (such as Kevlar) have major uses as stronger, lighter-weight replacements for metals and other materials in various structural applications, such as body armor (football helmets, bulletproof vests, etc.) and auto and airplane parts. Uses of side-chain LCPs include electro-optic devices. Mixtures with LCPs are important in modifying the ordering of a pure LCP and thus are important in industrial processing.

There are thousands of possible chemical structures in LCPs. A reasonably typical example of a LMW LC structure that appears dp times to make a backbone LCP is

$$[\text{-O-}\phi\text{-N=N-}\phi\text{-O-}(\text{CH}_2)_y\text{-}]_{dp}$$

← → ← →

rigid section semiflexible section

ϕ indicates a *para*-substituted benzene ring. $y \sim 0$ to 20. dp is also the degree of polymerization. The side chains of side-chain LCPs are similar LMW LC structures, but may have two semiflexible sections--one on either end of the rigid section.

The overlap of π orbitals in the aromatic, double, and triple bonds in a rigid section leads to the rigidity of that section. The *n*-alkyl chain section is partially flexible (semiflexible) since there are one *trans* and two *gauche* rotational energy minima for a carbon-carbon bond between methylene or methyl units in a given chain section.

THEORY

The theory used in this paper involves extension and refinement of earlier, very successful theories (Refs. 2-10) applied to LMW LCs. While the these earlier theories could have been used for longer molecules (such as backbone LCPs) by simply increasing the total numbers of rigid and semiflexible single sites (segments) in the molecule, the theory of this paper explicitly treats repeat units (where each repeat unit can have a rigid section and multiple semiflexible sections as discussed in the preceding "Introduction" section) and how these units repeat to make up the complete polymer molecule.

In the theory of this paper, the chemical structure of each molecule is divided into a sequence of connected sites (or segments) where these sites correspond to small groups of atoms (such as benzene rings and methylene groups). We then use a localized mean-field (LMF) simple-cubic (SC) lattice theory to study the packing of the molecules (segment by segment) in the system volume at a given pressure and temperature.

We use SC lattice theory since any orientation of a molecule or molecular part or bond can be decomposed into its x, y, and z components and mapped onto a SC lattice in a manner analogous to normal coordinate analysis in, for example, molecular spectroscopy. LMF means that there is a specific average neighborhood (of other molecular sites and empty space) in a given direction k around a given molecular site in a given local region in the system. These local regions are determined by the actual packing of the molecules in the system. The fact that the packing can be different for different directions k allows us to treat partial orientational ordering along a perferred axis. And, the treatment of local regions allows us to deal with partial positional ordering (see discussion in Refs. 4-7, 9-10).

The packing of the molecules is done mathematically using lattice combinatorial statistics to determine the analytic partition function Q for the system. (The generalized combinatorics used in the theory of this paper have been found to be quite accurate when compared with Monte Carlo computer simulations in at least one limiting case presently amenable to such simulations (see discussion in Ref. 4). Various continuum limits are taken in the theory of this paper.

The partition function Q and the resulting equations for static thermodynamic and molecular ordering properties are functions of the pressure P, temperature T, density ρ, lengths and shapes of the rigid and semiflexible sections of the molecules, net energy difference E_g between trans and gauche states, dipole moments, site-site polarizabilities and Lennard-Jones (12,6) potentials, degree of polymerization, and orientational and one-dimensional (smectic-A) positional orderings of the different rigid and semiflexible parts of the molecules. The Lennard-Jones (LJ) potentials are used to calculate repulsions and London dispersion attractions between different molecular sites, and the dipole moments and polarizabilities are used to calculate dipole/dipole and dipole/induced dipole interactions between different molecular sites. Each interaction in the theory of this paper depends explicitly on the intramolecular and intermolecular orientational and positional ordering of the specific molecular sites involved in the interaction.

There are no ad hoc or arbitrarily adjustable parameters in this theory. All variables used in the theory of this paper are taken from experimental data for atoms or small groups of atoms or are calculated in the theory.

The theory used in this paper has been derived in detail elsewhere (Refs. 11-13) and involves (Refs. 11-16) extension and refinement of earlier, very successful theories (Refs. 2-10) for LCs and their mixtures. Due to the summary nature of this paper, we note only the changes made in this paper (to the LC equations of these earlier theories) in order to treat backbone LCPs, side-chain LCPs, and mixtures with backbone LCPs in this paper.

SPECIFIC THEORY FOR BACKBONE LCPS

This theory treats backbone LCPs in nematic, smectic-A1, and smectic-Ad LC phases and in the isotropic liquid phase. In the LC phases, the long axes of the molecules tend to orient parallel to a preferred axis. In the smectic-A LC phases, the molecules also have one-dimensional (1-D) positional alignment (along the preferred axis), such rigid sections pack with other rigid sections while semiflexible sections pack with other semiflexible sections. In the smectic-Ad LC phase, there is partial 1-D positional alignment. In the smectic-A1 LC phase, there is total 1-D positional alignment.

The equations in the theory of this paper for backbone

LCPs are derived in detail elsewhere (Ref. 11) and are the same as the equations of Ref. 7, except for the following changes. [Variables not defined in this paper have been previously defined in Ref. 7.]

$(r - 1)$ in Eqs. (4), (5), and (10) of Ref. 7 becomes $[r - (1/dp)]$ in the theory of this paper for backbone LCPs. B_i in Eq. (13) of Ref. 7 becomes $B_i = (1/dp) + x[2f(1 - P_{2i})/3)]$. η, τ, and ν in Ref. 7 become P_{2r}, P_{2f}, and P_{2i}, respectively. (These symbol changes for η, τ, and ν are changes in the actual symbols, but <u>not</u> in the definitions of the variables for which these symbols stand.) <u>v</u> in Eq. (15) of Ref. 7 becomes $v = a^2\{(2a/dp) + v_o^{1/3}[m - (2/dp)]\}$. d_L in Eq. (16) in Ref. 7 becomes $d_L = v_o^{1/3}\{r + f[(1 + 2P_{2i})/3]\} + [(a - v_o^{1/3})/dp]$.

The treatment of the flexibility of a semiflexible chain in Ref. 7 was significantly refined in Refs. 8-10: Thus, Eq. (14) of Ref. 7 is replaced in this paper by $P_{2i} = \langle(3\cos^2\psi - 1)\rangle/2 = 1 - 3u$, $2u = (\Sigma_\gamma\ 2u_\gamma f_\gamma)/(\Sigma_\gamma\ f_\gamma)$, $f = \Sigma_\gamma\ f_\gamma$, where f_γ is the number of semiflexible segments ($-CH_2-$ or $-CH_3$ groups) in the semiflexible-chain section γ of the molecule, $2u_\gamma = 2\zeta_2$ for $f_\gamma = 1$.

$2u_\gamma = \{(\Sigma_{j=1}^{2}\ Y_{1j}) + [(f_\gamma - 2)/2][\Sigma_{j=1}^{2}\ Y_{2j}]\}/f_\gamma$ and

$2u_\gamma = \{(\Sigma_{j=1}^{3}\ Y_{3j}) + [(f_\gamma - 3)/2][\Sigma_{j=1}^{2}\ Y_{2j}]\}/f_\gamma$

for even $f_\gamma \geq 2$ and for odd $f_\gamma \geq 2$, respectively.

$Y_{11} = 2(\zeta_1\zeta_2 + \zeta_2^2)/D_1$, $Y_{12} = 2(2\zeta_1\zeta_2 + \zeta_2^2)/D_1$,

$Y_{21} = Y_{22} = 2(\zeta_1^2 + 3\zeta_1\zeta_2 + 2\zeta_2^2)/D_2$,

$Y_{31} = 2(\zeta_1^2\zeta_2 + 3\zeta_1\zeta_2^2 + \zeta_2^3)/D_3$,

$Y_{32} = 2(2\zeta_1^2\zeta_2 + 4\zeta_1\zeta_2^2 + \zeta_2^3)/D_3$,

$Y_{33} = 6(\zeta_1^2\zeta_2 + \zeta_1\zeta_2^2)/D_3$,

$D_1 = \zeta_1^2 + 4\zeta_1\zeta_2 + 2\zeta_2^2$, $D_2 = 3\zeta_1^2 + 2(5\zeta_1\zeta_2 + 3\zeta_2^2)$,

$D_3 = \zeta_1{}^3 + 2(3\zeta_1{}^2\zeta_2 + 4\zeta_1\zeta_2{}^2 + \zeta_2{}^3)$,
$\zeta_1 = 1/(1 + 2\Lambda)$, $\zeta_2 = \Lambda/(1 + 2\Lambda)$, and $\Lambda = \exp[-E_g/(kT)]$.
In the limit dp → 1, the equations here for backbone LCPs reduce to the equations of Refs. 7 and 9-10 as applied to LMW LCs.

In the calculations for backbone LCPs in this paper, there is one semiflexible chain section per repeat unit. Thus in the above equations, $f = f_1$ and $2u = 2u_1$ for backbone LCPs in this paper, where f_1 and $2u_1$ are calculated using the equations given above for f_γ and $2u_\gamma$, respectively.

As in Ref. 7, various thermodynamic equations are obtained (after the manner of Refs. 2-3 and 5-6) from the partition function $\underline{Q}$, including (1) a pressure-volume-temperature (PVT) equation of state, and (2) and (3) equations that minimize the Gibbs free energy of the system with respect to P_{2r} (the average orientational order of the rigid sections of the molecules) and λ [the average 1-D positional order (i.e., smectic-A order) of the molecules], respectively, at constant $\underline{P}$ and $\underline{T}$. As in Ref. 7, these three specific equations are (in general) solved simultaneously (via numerical computer iteration) to obtain numerical values of the three independent variables ρ, P_{2r}, and λ in the various phases of the system at given $\underline{P}$ and $\underline{T}$, given the physical constraints $0 < \rho \leq 1$, $0 \leq P_{2r} \leq 1$, and $0 \leq \lambda \leq 1$.

SPECIFIC THEORY FOR PACKING OF SIDE CHAINS IN LCPS

In the theory of this paper for side-chain LCPs, we concentrate on the packing of the LC side chains (of the side-chain LCPs) in fully-interdigitated monolayer smectic-A and non-interdigitated bilayer smectic-A LC phases. In this theory for side-chain LCPs, there is one side-chain per repeat unit in the backbone of the LCP.

The equations in the theory of this paper for the packing of side chains in side-chain LCPs are derived in detail elsewhere (Ref. 12) and are the same as the equations of Ref. 7, except for the following changes. [Variables not defined in this paper have been previously defined in Ref. 7. Variables used for the LMW LCs in Ref. 7 are retained for the LC side-chains in the side-chain LCPs in this paper.]

B_i in Eq. (13) of Ref. 7 becomes $B_i = (1/2) + x[2f(1 - P_{2i})/3)]$ in the theory of this paper for side-chain LCPs. η, τ, and ν in Ref. 7 become P_{2r}, P_{2f}, and P_{2i}, respectively. (These symbol changes for η, τ, and ν are changes in the actual symbols, but <u>not</u> in the definitions of the variables for which these symbols stand.) <u>v</u> in Eq. (15) of Ref. 7 becomes $v = a^2[a + v_o^{1/3}(m - 1)]$. d_L in Eq. (16) in Ref. 7 becomes $d_L = v_o^{1/3}\{3 + r + f[(1 + 2P_{2i})/3]\} + 2(a - v_o^{1/3})$ for side chains packing in fully-interdigitated monolayer smectic-A LC phases. d_L in Eq. (16) in Ref. 7 becomes $d_L = 2v_o^{1/3}\{2 + r + f[(1 + 2P_{2i})/3]\} + 2(a - v_o^{1/3})$ for side chains packing in non-interdigitated bilayer smectic-A LC phases. $\lambda = 1$.

<u>a</u> in Eq. (15) of Ref. 7 becomes--in this theory for side-chain LCPs in this paper--the average separation distance between the centers of two first-neighbor molecular segments (sites) in neighboring side-chains. In this paper, $a = a'$ for side chains that pack with side

chains on the same molecule (i.e., non-interdigitated packing), and $a = a'/2$ for side chains of a molecule that interdigitate with (i.e., pack between) the side chains of other molecules. Here, $a' = v_o^{1/3}\{r_b + f_b[(1 + 2P_{2ib})/3]\}$.

r_b, f_b, P_{2ib}, E_{gb}, and $2u_b$ are variables dealing with the backbone in the side-chain LCPs and are the same as $\underline{r}$, $\underline{f}$, P_{2i}, E_g, and 2u, respectively, for a backbone LCP, except for the following changes: $f_b = f_{b1} + f_{b2}$, and $2u_b = (\Sigma_\gamma\ 2u_{b\gamma}f_{b\gamma})/(\Sigma_\gamma\ f_{b\gamma})$. $f_{b1} = f_{b2}$ and $f_{b1} = (f_{b2} + 1)$ for even and odd f_b, respectively.

The number $\underline{f}$ of semiflexible segments in a side chain is given by $f = f_s + f_t$. Here, $f_s = (f_1 + f_2)$ and is the number of semiflexible segments in the semiflexible spacer between the backbone and the rigid section of the side chain in the side-chain LCP. $f_1 = f_2$ and $f_1 = (f_2 + 1)$ for even and odd f_s, respectively. $f_t = f_3$ and is the number of semiflexible segments in the terminal chain section attached to the outer end of the rigid section in the side chain of the side-chain LCP. 2u and P_{2i} in this theory for side-chain LCPs are calculated using f_1, f_2, and f_3 in the equations for 2u and P_{2i}, respectively, in the preceding section "Specific Theory for Backbone LCPs".

The above treatments (Ref. 12) of the semiflexible sections in the backbone and side chains of a side-chain LCP arise from the intramolecular coupling of the orientational and positional ordering of the backbone to the orientational and positional ordering of the side-chains. In this particular theory here for the packing of side chains (of side-chain LCPs) in smectic-A phases, the simplifying (but physically reasonable) assumption is made that side chains pack with other side chains while backbones pack with other backbones. Thus, this theory may be viewed as calculating upper bounds for the efficient packing of backbones and side chains of side-chain LCPs.

As in Ref. 7, various thermodynamic equations are obtained (after the manner of Refs. 2-3 and 5-6) from the partition function $\underline{Q}$, including an equation that minimizes the Gibbs free energy of the system with respect to P_{2r} (the average orientational order of the rigid sections of the side chains) at constant $\underline{P}$ and $\underline{T}$. After the manner of Ref. 7, this specific equation is solved (via numerical computer iteration) to obtain numerical values of the independent variable P_{2r} in the various phases of the system at given $\underline{P}$ and $\underline{T}$, given the physical constraints $0 \leq P_{2r} \leq 1$.

SPECIFIC THEORY FOR MIXTURES WITH BACKBONE LCPS

This theory treats binary mixtures in the nematic LC phase and the isotropic liquid phase. In these mixtures, Component 1 (C1) is a backbone LCP and Component 2 (C2) can be either polymeric or non-polymeric and either LC or non-LC. In this theory, there is one semiflexible section in the repeat unit of each component.

The equations for these binary mixtures (Refs. 13 and 15) are derived in detail elsewhere (Ref. 13) and are the same as the equations of Ref. 2, except for the following changes. [Variables not defined in this paper have been previously defined in Refs. 2 and 7.]

λ and Ψ in Ref. 2 become $\underline{1}$ and $\underline{2}$, respectively, in this paper here. $(r_\lambda - 1)$ and $(r_\Psi - 1)$ in Ref. 2 become $[r_1 - (1/dp_1)]$ and $[r_2 - (1/dp_2)]$, respectively. B_λ and B_Ψ in Ref. 2 become $B_1 = (1/dp_1) + [2f(1 - P_{2i1})/3)]$ and $B_2 = (1/dp_2) + [2f(1 - P_{2i2})/3)]$, respectively. η_λ, η_Ψ, τ_λ, τ_Ψ, ν_λ, and ν_Ψ in Ref. 2 become P_{2r1}, P_{2r2}, P_{2f1}, P_{2f2}, P_{2i1}, and P_{2i2}, respectively. f_1, f_2, dp_1, dp_2, E_{g1}, E_{g2}, $2u_1$, $2u_2$, P_{2i1}, and P_{2i2} are defined in this mixture theory for C1 and C2 in the same manner as $\underline{f}$, dp, E_g, 2u, and P_{2i}, respectively, are defined for pure backbone LCPs. $2u_1$, $2u_2$, P_{2i1}, and P_{2i2} are calculated using f_1, f_2, E_{g1}, E_{g2} in the equations for 2u and P_{2i}, respectively, in the preceding section "Specific Theory for Backbone LCPs".

The treatment of segmental intermolecular interactions in Ref. 2 has been significantly refined (after the manner of Ref. 7) in Ref. 13: In the following, $\underline{i}$ and $\underline{k}$ can each take the values 1 or 2. $\omega_{citk\parallel} = \omega_{citk\perp} = \omega_{citk}$. $\omega_{titk\parallel} = \omega_{titk\perp} = \omega_{titk}$. Each $\omega_{yizk} = \Sigma_{j=1}^{3} \omega_{yizkj}$. $\omega_{yizk1} = 4\epsilon_{yizk}[(a_\sigma/a)^{12} - (a_\sigma/a)^6]$. $\epsilon_{yizk} = (\epsilon_{yi}\epsilon_{zk})^{1/2}$. $\omega_{cick1\parallel} = \omega_{cick1\perp}$. ω_{yizk2} and ω_{yizk3} are calculated (after the manner of Ref. 7) using Eqs. (13.5-3) and (1.3-8), respectively, of Ref. 17(a) using values of μ_{D1}, μ_{D2}, α_{c1}, α_{c2}, α_{t1}, and α_{t2}, where these latter six variables are defined for pure C1 and pure C2 in this paper in the same manner as μ_D, α_c, and α_t are defined in Ref. 7. $\omega_{cick2\parallel} = \omega_{cick2\perp} = -(\mu_{Di}^2\alpha_{ck} + \mu_{Dk}^2\alpha_{ci})/[2a^6(r - 2)^2]$. $\omega_{citk2} = -\mu_{Di}^2\alpha_{tk}/[2a^6(r - 2)^2]$. $\omega_{cick3\parallel} = -\mu_{di}\mu_{dk}/\{2[a(r - 2)]^3\}$. $\omega_{titk2} = \omega_{cick3\perp} = \omega_{citk3} = \omega_{titk3} = 0$. $v = (x_1a^2\{(2a/dp_1) + v_o^{1/3}[m - (2/dp_1)]\} + x_2a^2\{(2a/dp_2) + v_o^{1/3}[m - (2/dp_2)]\})/(x_1m_1 + x_2m_2)$. In this paper, the global mole fractions X_1

and X_2 in the mixture are defined in terms of the local mole fractions x_1 and x_2 by $X_1 = x_1dp_2/(x_1dp_2 + x_2dp_1)$ and $X_2 = 1 - X_1$.

As in Ref. 7, various thermodynamic equations are obtained (after the manner of Refs. 2-3 and 5-6) from the partition function Q, including (1) a pressure-volume-temperature (PVT) equation of state, and (2) and (3) equations that minimize the Gibbs free energy of the system with respect to P_{2r1} and P_{2r2} in the various phases at constant P and T. As in Ref. 7, these three specific equations are (in general) solved simultaneously (via numerical computer iteration) to obtain numerical values of the three independent variables ρ, P_{2r1}, and P_{2r2} in the various phases of the system at given P and T, given the physical constraints $0 < \rho \leq 1$, $0 \leq P_{2r1} \leq 1$, and $0 \leq P_{2r2} \leq 1$.

RESULTS AND DISCUSSION

This paper reports theoretical predictions and explanations for some magnitudes and trends in thermodynamic and molecular ordering properties as a function of details of molecule chemical structure for backbone LCPs, side-chain LCPs, and mixtures with backbone LCPs. The theoretical results in this paper were calculated using the theories outlined in the preceding "Theory" section. These theoretical results are found to be physically reasonable and in agreement with available experimental data.

RESULTS FOR BACKBONE LCPS

Theoretical results for backbone LCPs are shown here as a function of the degree of polymerization. Table I shows the effect of the degree of polymerization dp on some properties at the transition between the nematic (N) LC phase and the isotropic (I) liquid phase for a backbone LCP. (The N phase is the lower-T phase, and the I phase is the higher-T phase.)

TABLE I. Some transition properties vs. dp for a backbone LCP with N and I phases.

dp	T_{N-I} (K)	P_{2r}
1	311.7	0.6186
5	485.4	0.6835
10	523.3	0.6945
50	558.0	0.7041
10^2	562.7	0.7053
10^3	566.9	0.7065
10^4	567.4	0.7066
10^5	567.4	0.7066

T_{N-I} is the transition temperature, and P_{2r} is the average orientational order for a rigid section of the LCP in the N phase at the transition. $P_{2r} = \langle(3 \cos^2\theta_r - 1)\rangle/2$, where θ_r is the angle between the long axis of a rigid section and the preferred axis or orientation for this rigid section.

From experimental data [Refs. 17(b)-21] for atoms or small groups of atoms, the input variables (for definitions, see Ref. 7) for the example LCP of Table I were estimated (Ref. 11) after the manner of Ref. 7 to be $r = 5$, $f = 3$, $\epsilon_{cc}/k = 290$ K, $\epsilon_{tt}/k = 150$ K, $\mu_D = 1.45$ D, $\alpha_c' = 32\times10^{-24}$ cm^3, and $\alpha_t = 2\times10^{-24}$ cm^3. These variables are appropriate for a LCP with a molecule chemical structure of $[\text{-O-}\phi\text{-}\phi\text{-}\phi\text{-CH}_2\text{-(CH}_2)_3\text{-}]_{dp}$. P = 1 atm. All calculations in this paper (as in Ref. 7) use $E_g/k = 250$ K.

We have chosen the backbone LCP of Table I since it is about the simplest backbone LCP with a longitudinal dipole in the rigid section of the repeat unit. This particular repeat unit has about the smallest longitudinal dipole that one could have. By choosing a repeat unit with a dipole, we have of course emphasized the fact that the theory of this paper can treat dipolar forces.

In Table I, the transition properties increase as dp increases, with the value of a property tending to asymptote as dp → ~ 100. This trend is in good agreement with experimental results (see, for example, Ref. 22) for numerous backbone LCPs.

It makes sense physically that adding another repeat unit to the backbone makes less relative change in the length (and other properties) of the LCP as the length increases. It is clear from Table I that the effects of polydispersity on system properties can be large for dp less than the asymptotic value, while polydispersities in the dp range greater than this asymptotic value have less effect on system properties.

Calculations of other thermodynamic and molecular ordering properties (including odd-even effects) for various backbone LCPs in the nematic, smectic-A1, and smectic-Ad LC phases and in the isotropic liquid phase as a function of different features of the chemical structures are presented in other papers (Refs. 11 and 16) and therefore are not detailed here.

RESULTS FOR SIDE-CHAIN LCPS

This section gives some theoretical predictions and physically reasonable explanations for the effect of varying the chemical structure in the side chain of a side-chain LCP on the transition of the side chains from packing in a monolayer smectic-A (SA) (i.e., a SA1 phase) to packing in a bilayer SA phase (i.e., a SA2 phase). In the monolayer SA1 phase, the side chains on a molecule fully interdigitate with (i.e., pack between) the side chains of other molecules. In the SA2 phase, the side chains on a molecule pack only with neighboring side chains on the same molecule. The SA1 phase is the lower-*T* phase, and the SA2 phase is the higher-*T* phase. Specifically, the number 2y of methylene or methyl groups in the semiflexible sections in the side chain of an example side-chain LCP is varied in Table II.

TABLE II. Some SA1-SA2 transition *T* vs. *y* in a side-chain LCP.

y	$T_{SA1-SA2}$ (K)
3	464.1
4	502.1
5	528.5
6	547.7

From experimental data [Refs. 17(b)-21] for atoms or small groups of atoms, the input variables (for definitions, see Ref. 7 and the preceding theory section of this paper for side-chain LCPs) for the example LCP of Table II were estimated (Ref. 12) after the manner of Refs. 2 and 7 to be $r = 5$, $f = 2y$, $\epsilon_{cc}/k = 283$ K, $\epsilon_{tt}/k = 150$ K, $\mu_D = 0$, $E_g/k = 250$ K, $r_b = 2$, $f_b = 4$, $E_{gb}/k = 250$ K. These variables are appropriate for a side-chain LCP with a backbone chemical structure of $[-\underset{|}{\mathrm{C}}\mathrm{H}-(\mathrm{CH}_2)_5-]_{100}$ and a side-chain chemical structure of $-\mathrm{CH}_2-(\mathrm{CH}_2)_y-\mathrm{CH}_2-\phi-\mathrm{N}{=}\mathrm{N}-\phi-\mathrm{CH}_2-(\mathrm{CH}_2)_{(y-1)}-\mathrm{CH}_3$. $P = 1$ atm.

We have chosen the side-chain LCP of Table II since it has about the simplest backbone chemical structure and has a very simple side-chain chemical structure. By choosing a side-chain LCP with no dipoles, we have of course emphasized the fact that the transition of the side chains between packing in a monolayer SA1 phase to packing in the bilayer SA2 phase does not require dipolar forces.

In Table II, the SA1 phase becomes more stable at higher $\underline{T}$ as the side-chain becomes longer. [Calculations (Ref. 12) using the theory of this paper predict that different trends can occur, depending on the chemical structures of the backbone and side chains in side-chain LCPs.]

In general, energy favors the SA1 phase, and entropy favors the SA2 phase. That is, the side chains are closer to each other in the SA1 phase (fully interdigitated phase) and have more favorable attractive energies than in the SA2 phase (non-interdigitated phase). [This statement is true for the SA1 phase if (as in Table II) the backbone chemical structure has been chosen such that the side chains are far enough apart so that they do not experience the strongly repulsive parts of their potentials when they are interdigitated in a SA1 phase.] In the SA2 phase, the side chains are farther from each other and thus have more entropy (disorder) than in the SA1 phase.

As discussed in detail in Ref. 12, the relative stabilities of the SA1 and SA2 phases are an extremely sensitive function of the specific chemical structures of the backbone and the side chains of side-chain LCPs and of how the flexibility, packing, and intermolecular forces of these structures change as a function of $\underline{T}$ and $\underline{P}$. While some side-chain LCPs (such as that illustrated in Table II) can exhibit both SA1 and SA2 packing in ranges of $\underline{T}$ and $\underline{P}$ that are reasonably accessible to experiment, other side-chain LCPs are predicted to exhibit (Ref. 12) only SA1 packing or only SA2 packing in such ranges of $\underline{T}$ and $\underline{P}$.

RESULTS FOR MIXTURES WITH BACKBONE LCPS

Theoretical predictions and explanations are reported for binary mixtures of a backbone LCP [Component 1 (C1)] with a second compound [Component 2 (C2)], which may be either polymeric or non-polymeric and either LC or non-LC.

Effect of Molecular Structure of Component 2

The effect of the molecular structure of Component 2 (C2) in a binary mixture with a backbone LCP [Component 1 (C1)] is illustrated in this section. Table III shows theoretical results calculated for binary mixtures of a backbone LCP and three different C2 molecular structures at the nematic-to-isotropic (N-I) transition. These three C2 compounds are a non-LC LMW compound, a non-LC polymer, and a LC LMW compound.

TABLE III. Mole fractions of Component 2 of different molecular structures in the coexisting N phase vs. reduced T in binary mixtures with a backbone LCP.

	M1 (non-LC LMW)	M2 (non-LC polymer)	M3 (LC LMW)
$T/(T_{N-I})_1$	X_{2N}	X_{2N}	X_{2N}
1.000	0.0000	0.0000	0.0000
0.999	0.0192	0.0009	0.0641
0.990	0.1638	0.0091	0.4093
0.970	0.3692	0.0274	0.6811
0.950	0.4928	0.0461	0.7855
0.925	0.5918	0.0700	0.8508
0.900	0.6579	0.0944	0.8878

Since the N-I transition is a (weakly) first-order transition (i.e., has small, but finite changes in density, energy, enthalpy, entropy, etc.), there is a two-phase region (i.e., a range of mole fraction X_2 of C2 in which both phases (N and I) coexist simultaneously). X_{2N} and X_{2I} are the mole fractions of C2 in the coexisting N and I phases, respectively, at a given reduced T given by $T/(T_{N-I})_1$, where $(T_{N-I})_1$ is the N-I transition T for pure C1. Due to space constraints, only X_{2N} is listed for each mixture in Table III.

The calculations in Table III are for mixtures in which the molecules interact with each other through only steric (i.e., hard, or infinitely large) repulsions. That is, all $\omega_{yizk} = 0$ (see the preceding theory section for mixtures with backbone LCPs). P = 1371.8 atm. As is well-known (Refs. 3 and 5-7), condensed phases can only exist at higher P and/or lower T in theories in which the molecules interact only through hard-repulsive forces than in theories in which the molecules also interact through attractive forces.

The molecules are all sequences of connected segments, with each segment being of unit dimensions. Results are shown for a backbone LCP C1 with a repeat unit of 4 rigid segments and then 3 semiflexible segments; thus, $r_1 = 4$ and $f_1 = 3$. $E_{g1}/k = 250$ K. In all three mixtures in Table III, $dp_1 = 100$.

Also, $E_{g2}/k = 250$ K for C2 in all three mixtures in Table III. In Mixtures 1 and 2 (M1 and M2) in Table III, the C2 repeat unit has 2 rigid segments and then 4 semiflexible segments; thus, $r_2 = 2$ and $f_2 = 4$ in M1 and M2. $dp_2 = 1$ in M1, and $dp_2 = 100$ in M2. In M3 in Table III, C2 has 4 rigid segments and 2 semiflexible segments; thus, $r_2 = 4$ and $f_2 = 2$ in M3. $dp_2 = 1$ in M3. These input variables for C2 in M1 and M2 are consistent

(Refs. 2 and 7) for a non-LC LMW alkyl chain and a non-LC polymeric alkyl chain, respectively. These input variables for C2 in M3 are consistent (Ref. 7) for a LMW LC.

Each of the three C2 compounds in Table III tends to disrupt the orientational ordering of the backbone LCP, thus lowering the T_{N-I} of the mixture. This result is consistent with calculated and experimental results for LMW LC systems (see Ref. 2).

Table III illustrates the effect of the flexibility of C2 on the binary mixture with a backbone LCP. As seen in Table III, a smaller mole fraction X_2 of the more flexible C2, whether LMW or polymeric (see M1 and M2), is required to achieve the same reduced transition $\underline{T}$ [i.e., $T/(T_{N-I})_1$] of the backbone LCP C1 than is required with the more rigid C2 (see M3). That is, the more flexible (non-LC) C2 is more effective than the more rigid (LC) C2 in disrupting the orientational order of the backbone LCP C1. (Even though C2 in M3 is LC itself, it is shorter and thus less ordered than the backbone LCP C1 and therefore tends to disrupt the orientational ordering of C1 somewhat.) It makes sense physically that a more flexible C2 disrupts the orientational order more than a more rigid C2, since a more flexible compound has less tendency to orientationally order itself than a more rigid compound.

Table III also illustrates the effect of the degree of polymerization of a non-LC C2 on the binary mixture with a backbone LCP. As seen in Table III, a smaller mole fraction X_2 of the non-LC polymer C2 in M2 than of the non-LC LMW C2 in M1 is required to achieve the same reduced transition T of the backbone LCP C1. That is, the non-LC polymer C2 is more effective than the non-LC LMW C2 in disrupting the orientational order of the backbone LCP C1. This result makes sense physically, since it is easier for the long chains of the non-LC polymer C2 than the short chains of the non-LC LMW C2 to disrupt the orientational order of a backbone LCP C1.

As seen in Table III and later, the coexistence curves for the mixtures of a backbone LCP C1 and a non-LC C2 (or a less-ordered LC C2) are not straight lines in reduced-T vs. X_2 phase space, but rather are curved in a somewhat concave-downward (i.e., concave toward lower-T) manner. These curvatures are much more pronounced if one component is a polymer and the other component is a LMW compound (as is the case in M1 and M3 in Table III). Thus, these curvatures are more pronounced if there is a larger difference between the lengths and shapes of the molecules. That is, if C2 is of a rather different length and shape than C1, the effect of adding more C2 is noticeably not linear. This result makes sense physically: For example, if (as in M1 and M3 in Table III) C2 is of a shorter length than C1, more C2 has to be added before the longer C1 molecules are as effectively affected as in the case in which the molecules have more similar lengths.

We have chosen the example systems of Table III to show that hard repulsions (specifically, the effects of the steric packing of molecules of different lengths and shapes) are sufficient to generate the curvatures of these coexistence curves. Thus, attractive forces (including dipolar forces) are not required for these curvatures.

The theory of this paper appears to be the first theory to generate and explain these curvatures, particularly for larger reduced-T. These curvatures are seen experimentally (see, for example, Ref. 23).

It is worth noting, in passing, that the theory of this paper predicts that if the pure C2 orientationally orders more than the pure C1, adding C2 to C1 will increase the N-I transition T of C1, as has been seen in Ref. 2 for calculations with LMW systems.

The theory of this paper can be used to perform calculations at smaller reduced-T, where the width of the two-phase region rapidly enlarges as T decreases in some experimental systems. Since earlier theories [such as that of Flory (see Ref. 24)] have been adequate to account for this enlargement of the two-phase region, we do not belabor the point in this paper, but rather concentrate (as discussed above) on the results of the theory of this paper at larger reduced-T.

Effect of Chemical Structure of the Backbone LCP

The effect of the chemical structure of a backbone LCP [Component 1 (C1)] in a binary mixture with a non-LC LMW compound [Component 2 (C2)] is illustrated in this section. Table IV shows theoretical results calculated for binary mixtures of a non-LC LMW C2 with backbone LCPs of different chemical structures at the nematic-to-isotropic (N-I) transition. The backbone LCP C1 has no dipole in Mixture 1 (M1), but has relatively large dipolar forces in Mixture 2 (M2).

X_{2N} and X_{2I} are the mole fractions of C2 in the coexisting N and I phases, respectively, at a given reduced T given by $T/(T_{N-I})_1$, where $(T_{N-I})_1$ is the N-I transition T for pure C1.

The calculations in Table IV are for mixtures in which the molecules interact with each other through these site-site interactions: soft (finite-sized) repulsions and

London dispersion attractions, as well as steric (i.e., hard, or infinitely large) repulsions. These interactions are calculated using site-site Lennard-Jones (12,6) potentials as explained in the preceding "Theory" section. In addition, M2 also has site-site dipolar forces (dipole/dipole and dipole/induced dipole interactions). P = 1 atm.

TABLE IV. Mole fractions of a non-LC LMW Component 2 in the coexisting N and I phases vs. reduced T in binary mixtures with a backbone LCP with different dipolar forces.

	M1 (nondipolar LCP)		M2 (dipolar LCP)	
$T/(T_{N-I})_1$	X_{2N}	X_{2I}	X_{2N}	X_{2I}
1.000	0.0000	0.0000	0.0000	0.0000
0.999	0.0329	0.0477	0.8542	0.9647
0.990	0.2482	0.3315	0.8533	0.9652
0.975	0.4819	0.5937	0.8509	0.9665
0.950	0.5937	0.7059	0.8481	0.9677
0.925	0.6713	0.7801	0.8439	0.9691
0.900	0.7176	0.8237	0.8389	0.9704

From experimental data [Refs. 17(b)-21] for atoms or small groups of atoms, the input variables (for definitions, see Refs. 2 and 7 and the preceding theory section for mixtures with backbone LCPs) for the example mixtures of Table IV were estimated (Ref. 13) after the manner of Refs. 2 and 7 to be $r_1 = 4$, $f_1 = 3$, $dp_1 = 100$, $E_{g1}/k = 250$ K, $\epsilon_{c1c1}/k = 300$ K, and $\epsilon_{t1t1}/k = 150$ K for C1 in both mixtures. $\mu_{D1} = 0$ for C1 in M1. In M2, $\mu_{D1} = 5.2$ D, $\alpha'_{c1} = 24\times10^{-24}$ cm^3, and $\alpha_{t1} = 2\times10^{-24}$ cm^3 for C2. These variables are appropriate for a backbone LCP C1 with a repeat unit of $[\text{-CH}_2\text{-}\phi\text{-}\phi\text{-CH}_2\text{-(CH}_2)_3\text{-}]_{100}$ in both mixtures, where dipolar forces of the order of those in the rigid section $[\text{-O-}\phi\text{-}\phi\text{-C=N-}]$ have also been added to the rigid section of the repeat unit of the backbone LCP C1 in M2. This particular assignment of variables for C1 allows us to isolate the effect of adding longitudinal dipolar forces to the backbone LCP C1 in Table IV.

In both mixtures, $r_2 = 2$, $f_2 = 0$, $dp_2 = 1$, $E_{g2}/k = 250$ K, $\epsilon_{c2c2}/k = \epsilon_{t2t2}/k = 150$ K, $\mu_D = 0$, and $\alpha'_{c2} = \alpha_{t2} = 2\times10^{-24}$ cm^3 for C2. These variables are appropriate for a non-LC LMW C2 with a chemical structure of $CH_3\text{-}CH_3$.

As in Table III, the non-LC LMW C2 tends to disrupt the orientational ordering of the backbone LCP in each mixture in Table IV, thus lowering the T_{N-I} of each mixture.

Table IV illustrates the effect of the longitudinal dipolar forces in a backbone LCP C1 on the binary mixture with a non-LC LMW C2. As seen in Table IV, a smaller mole fraction X_2 of this C2 is required to achieve the same reduced transition $\underline{T}$ [i.e., $T/(T_{N-I})_1$] of the backbone LCP C1 if C1 has no dipolar forces (see M1) than if C1 has dipolar forces (see M2). That is, more of a non-LC LMW

C2 is required to disrupt the orientational order of the backbone LCP C1 if C1 has a longitudinal dipole in the repeat unit than if C1 has no dipolar forces. This result makes sense physically, since a longitudinal dipole in the rigid section of the repeat unit of a backbone LCP can pull the rigid sections closer together and therefore orient these rigid sections more, thus making it more difficult for a non-LC LMW C2 to disrupt the orientational ordering of the backbone LCP molecules.

CONCLUDING REMARKS

This paper has presented a summary of some results (especially general trends) calculated using new theories for backbone LCPs, for side-chain LCPs, and for mixtures with backbone LCPs. (These theories for LCPs are extensions and refinements of earlier, very successful theories applied to LMW LCs.)

These new LCP theories predict and explain thermodyanamic and molecular ordering properties of these systems as a function of the different features of the molecule chemical structures and their packing. There are no ad hoc or arbitraily adjustable parameters in these theories. To emphasize the predictive ability of these LCP theories, the molcule chemical structures chosen for study in this paper have not yet (to the author's knowledge) been synthesized.

While constraints on the summary nature of this paper prohibit an exhaustive comparison of results calculated from the LCP theories of this paper and experimental results, we do note that the trends calculated for LCPs in this paper are physically reasonable and are in agreement with available experimental data. Furthermore, a comparison of the magnitudes of various thermodynamic and molecular ordering properties calculated for the LCP systems of this paper with the magnitudes of these properties for existing LCP systems indicates that the calculated results in this paper can be expected to be rather accurate qualitatively and semiquantitatively (and in some cases, also probably quantitatively). (See Refs. 11-13 for a more detailed comparison of some results for existing LCP systems calculated using the LCP theories of this paper with experimental results for these systems.)

The theories for LCPs in this paper have also been extended (Ref. 25) to study combined LCPs. [For experimental examples of combined LCPs, see Ref. 26 and references therein.] The theories of this paper are in the process of being extended to treat mixtures with side-chain and combined LCPs.

These theories of this paper have been used to design (atom-by-atom, bond-by-bond) new LCPs and new solvents for LCPs (Ref. 27).

ACKNOWLEDGMENT

This research was supported by the U. S. Department of Energy.

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